IJARSCT

ISSN (Online) 2581-9429

International Journal of Advanced Research in Science, Communication and Technology (IJARSCT)

Impact Factor: 5.731

Volume 12, Issue 4, December 2021

Eco- Friendly Applications in Presence of Biosynthesized Metal Nanoparticles

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Abstract: *Green chemistry has proven to be an effective way to synthesize metal nanoparticles. Nanoparticles are very important for the development of sustainable technology for the future, for humans and the environment. The synthesis of nanoparticles from plants is a green chemical approach that combines nanotechnology and plant biotechnology. The plant extract is used for the bio-reduction of metal ion to produce nanoparticles. Plant metabolites have been shown to play an important role in reducing metal ions to nanoparticles and aiding their subsequent stability. Conventional methods for synthesis of nanoparticles uses harmful chemicals, generate serious attention to the development of ecological processes. Therefore, green synthesis uses extracts from biological sources from plant sources, which are superior to conventional methods. Over the past decade, it has been shown that many biological systems, including plant extract such as Steams, leaves, latex, flower, seeds can convert inorganic metal ion into metal nanoparticles. The many plants and plant parts have been used successfully in the synthesis of several green Metal nanoparticles such as Ag, Cu, Fe, Au, Pd Nanoparticles have been confirmed by various instrumental techniques. NPs are widely used in areas such as magnetic devices, photocatalysts, microelectronic devices, anti-corrosion coatings, biomedical and electrocatalysts. Here we report the biosynthesis of FeNPs and their catalytic activity was tested for degradation kinetics for Malachite green dye (MG).*

Keywords: Nanotechnology, Biosynthesis, Metal Nanoparticles, Characterization, Catalytic applications

I. Introduction

The environmental impact of colorants is a concern over the last few decades. Industries such as textile, leather, paper, plastic and pharmaceutical produce a great amount of waste water contaminated with dyes in the world [1][2]. Among all synthetic dyes, azo dyes are the largest and most important class of dye for industrial application [3]. The presence of dyes not only highly colors the effluent even at low concentration; it also causes environmental problems due to their toxic and carcinogenic characteristics [4].

Azo dyes are difficultly degraded by conventional treatment methods because of their complex structure and stability. The different treatment methods such as adsorption and flocculation are not efficient because they generate solid waste; this creating another environmental problem requires further treatment [5]. Among various treatment methods, advance oxidation processes (AOR) are considered as one of the most effective methods to degrade azo dyes, which involves the generation of powerful oxidizing species such as sulfate radicals (SO_4^-) that attack the dye molecule [6], and degrade into harmless products. The advanced oxidation process (AOP) is the name given to several oxidation methods that are based on the generation of strong free radicals for destroying organic pollutants present in anthropogenic sources. In the past years, persulfate such as peroxomonosulphate (PMS, HSO_5^-) and peroxodisulfate (PDS, $S_2O_8^{2-}$) have attracted increasing attention because they show more stability than hydrogen peroxide. Furthermore, persulfate and their product (SO_4^{-2}) have the least effect on natural organisms[7]. Additionally, the sulfate radical (E^0 =2.5-3.1v) generated in activated persulfate systems is more selective than the hydroxyl radical (E^0= 1.8-2.7 v) for the degradation of organic compounds with carbon-carbon double bond and aromatic rings[8].Thermal radiation[9]. U.V. light[10] and transition metal[11] are the main technologies for persulfate activation. Moreover, the higher energy needs for thermal, U.V. light radiation and the risk of secondary pollutants compel further application of these methods. Therefore, it is a great interest to develop low cost, highly effective methods for the activation of persulfate for dye removal processes. Nanoscale iron particles are recently gaining great interest in environmental remediation circles. One of the prominent applications in this regard is the removal of organic and inorganic pollutants from aqueous solutions [1,2]. The nano-scale size offers high surface area and high surface reactivity. The shape and size of nanoparticles are important parameters in the manufacture, processing and applications due to high surface area and high surface reactivity, ion delivery or contact. Also, physical properties such as shape, composition, load, and solubility can change their behavior unpredictably [6].

Biosynthesis of iron nanoparticles using microorganism and plant extract [11] have been suggested as possible eco-friendly alternative to chemical and physical methods. Indian greeneries are the chief and cheap source of medicinal plants and plant products.

Here, we have developed a rapid, eco-friendly and convenient green route for the synthesis of FeNPs from their salt using leaf extract of Indian medicinal plant namely *A. indica*. *A. Indica* commonly known as neem belongs to meliaceae family. Synthesized FeNPs were then used for the degradation of a Malachite green dye solution to test their dye degradation performance. Malachite Green is classified in the dye industry as triarylmethane dye and used as a dye for materials such as silk, paper and leather. In the present study, the applicability of *A.Indica*(which is rich in phenol, flavonoid, and terpenoids, capable of reducing metal ions and stabilizing the resultant NPs) was explored in the synthesis of FeNPs.

II. Experimental

2.1 Material and Method

Peroxodisulphate (E. Merck), Ferric chloride (E. Merck), Malachite green. and other reagents employed analytical grade. Azadirachta Indica (Neem) leaves were collected from Kota (Rajasthan) India. Fresh and clean 10 gm Neem leaves were stirred on a magnetic stirrer with 50 ml distilled water at 80^{O}C. After 20 minutes neem extract filtered through Whatman filter paper and store in refrigerator (4^{O}C) for further experiments. Double distilled water was used throughout the study.ss

2.2 Characterization Techniques

Characterization of synthesized nanoparticles is significant to understand the synthesis process and morphology of particles. The formation of FeNPs, preliminary confirmed by U.V. visible spectroscopy by sampling the reaction mixture at different intervals of time and maximum absorption spectra were obtained in a range of wavelengths between 200-450 nm using (U.V 3000^{+} LAB.INDIA) double beam spectrophotometer.

III. Synthesis of Iron Nanoparticles

1.0 x10^{-3}mole l^{-1} solution of aqueous ferric chloride ($FeCl_2.4H_2O$) containing round flask heated at 80^{O}C on magnetic stirrer then 10 ml neem leaf extract was drop-wise added. The color of the reaction mixture black. The resulting solution was centrifuged for 15 minutes and the obtained supernatant was placed at 4^{O}C temperature.

IV. Kinetic Measurements:

The oxidative degradation of malachite green in FeNPs/PDS septum was carried out with the desired concentration of reactants in Stoppard Erlenmeyer flask at 30^{O}C temperature. The reaction was initiated by adding the known volume of the PMS solution. The rate of degradation was monitored by the absorbance of MG measured spectrophotometrically at max 617 nm with a regular interval of time. The kinetic plots for the rate constant were measured under pseudo-first-order conditions, which are obtained by plotting log absorbance versus time, and plots were linear, indicates pseudo-first-order kinetics.

V. RESULTS AND DISCUSSION

5.1 Characterization of Iron Nanoparticles

The biosynthesis of FeNPs has confirmed the color of dispersion changed from bright yellow to brownish-black shown in fig.1(a), indicates the reduction of Fe^{+2} into Fe^{0} particles can impart such color. The recent studies report that the optical properties of metal nanoparticles depend upon the size and shape, thus the optical response of nanoparticles can be controlled geometry and size of nanoparticles[26]. During the synthesis, the process is an aqueous solution; optical spectroscopy can be used as a primary tool for confirmation for metal nanoparticles. The absorption peak obtained maximum at 250 nm, which can be confidentially ascribed to SPR of Fe^{0} particles or FeNPs formation[28]. Fig.1 (b)

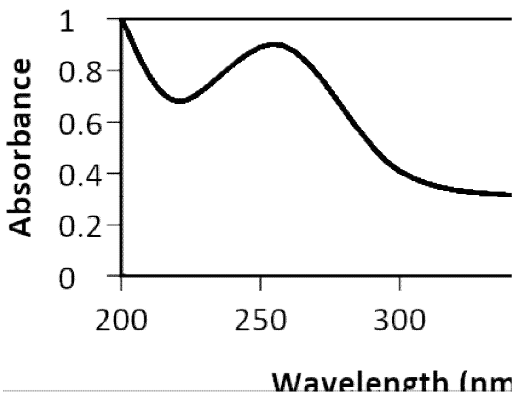

Figure 1-(a). Color change during the Fe nanoparticle synthesis process.
(b) U.V. visible spectra of Synthesized Fe nanoparticles

5.2 Effect of Experimental Conditions

A. Peroxodisulphate Dependence

Peroxodisulphate plays an important role as a source of sulfate radicals and activated by transition metals. Experiments runsto investigate the effect of various concentrations of PDS on MG degradation at a fixed concentration of other reactants and conditions. Increase the concentration of PDS contribute increases the degradation of MG. The positive correlation of PDS concentration with a degradation rate of MG suggests that PDS itself and either its secondary species supposed for the attack of dye molecules.

B. Dye Dependence

The initial concentration of MG varying from 1.0x 10^{-5} to 8.0x 10^{-5}mole l^{-1} at 30ºC and other reactant concentration constant. Results indicates that the degradation rate constant initially increases with increasing dye concentration and then tends towards a limiting value at a higher concentration of MG. The result illustrates that at high concentration of MG and constant PDS concentrations, the availability of So_4^{-2} radicals are constant so degradation rate was constant.

C. Effect of Iron Nanoparticles

The catalytic activity of synthesized FeNPs was evaluated in oxidative degradation of MG by PDS with different concentrations from $0.2x10^{-8}$ to $2.0x10^{-8}$ mole dm^3 at a fixed concentration of other reactants at temperature 30ºC. The rate of degradation of MG increases with an increasing concentration of FeNPs. At higher concentration of FeNPs would correspond to improvement to the decomposition of PDS to generate sulfate radicals. The catalytic activity of FeNPs are shown, a graph plotted between the different concentration of FeNPs and rate constants at three different temperatures. Fig.2

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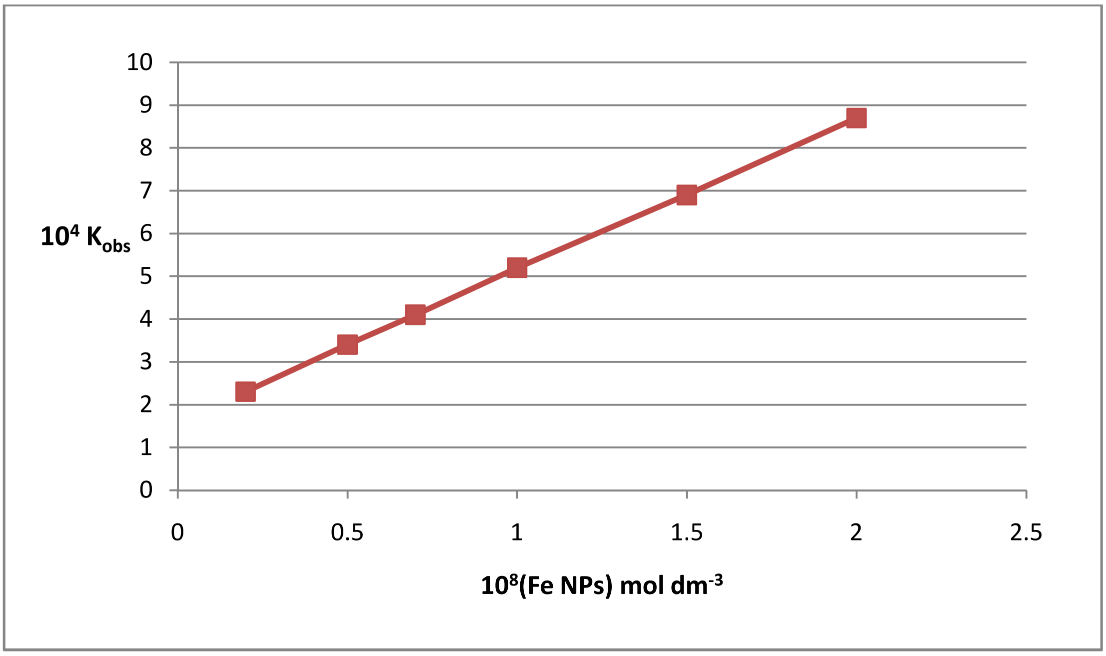

Figure 2: Effect on Fe-NPs on the degradation of MG

VI. Conclusion

The present research reports highly stable FeNPs synthesized by the Azardirachta Indica (Neem) leaf extract as an efficient, eco-friendly reducing as well as capping agent. Therefore, synthesized FeNPs have stability for one month at 4^{o}C temperature without any protecting gas. The green synthesized FeNPs were applied as a catalyst for the degradation of MG. The FeNPs shows good catalytic activity for the activation of PDS to generate sulfate radicals for degradation of MG into harmless products. The higher concentration of PDS, Catalyst, temperature promoted the degradation of MG in the FeNPs/ PDS system. The results recommended that FeNPs have good potential for fast dye degradation technology.

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